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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Hydroforming Catalyst and
Process of using the same

We, ESSO RESEARCH AND ENGINEERING COMPANY, formerly Standard Oil Development Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of microspherical particles of catalyst carriers or bases suitable for use in a hydroforming reaction. The present invention also relates to a process for hydroforming naphthas containing naphthenes in order to produce high anti-knock rating gasoline motor fuel constituents by contacting the feed naphthas at elevated temperatures and pressures with a hydroforming catalyst carried on a support so prepared.

Hydroforming is customarily defined as an operation in which a hydrocarbon, such as a naphtha, is contacted at elevated temperatures and pressures in the presence of added hydrogen with a solid catalyst material. There is no net consumption of hydrogen during the process ordinarily. The process involves (1) dehydrogenation of naphthenes to form the corresponding aromatics, (2) aromatization of paraffinic hydrocarbons, (3) isomerization of hydrocarbons wherein, for example, straight chain paraffins rearrange to form branch chain hydrocarbons and 5-membered carbo-cyclic rings are converted to 6-membered carbo-cyclic rings, and (4) hydro-cracking of paraffins. When properly operated, the process should yield a maximum of C₄+ hydrocarbons and minimum amounts of normally gaseous hydrocarbons and carbon.

The main object of the present invention is to provide a catalyst base for use in hydroforming which is adapted to promote the conversion of low octane hydrocarbon feed stock into gasoline constituents of high octane rating in good yields.

The present invention provides a method for the preparation of microspherical particles of catalyst carriers or bases suitable for use in a hydrocarbon hydroforming reaction carried out by the fluidised solid technique which comprises mixing an aqueous solution of aluminum sulphate with an aqueous solution of sodium aluminate, preferably also with a small proportion of an aqueous solution of sodium silicate, adjusting the pH of the mixture by the addition of acid or otherwise to between 9 and 10, preferably approximately 9.5, filtering off the precipitate formed reslurrying it with water and then spray drying the resulting slurry.

The catalyst carrier or base so formed may then be impregnated with a hydroforming catalyst such as platinum, palladium, molybdenum oxide, chromium oxide or titanium oxide.

In carrying out the hydroforming process itself, a naphtha feed stock is vaporized and heated to a temperature within the range of from about 900°—1050° F. These naphtha vapors contain substantial amounts of naphthenic hydrocarbons, some aromatics and some paraffins, and the feed stock is one which may be a virgin naphtha, a cracked naphtha, or a mixture of the two.

However, since the main feature of the present invention resides in the manner in which the base or spacing agent for the active component of the hydroforming catalyst is made, complete details as to the best method for preparing this base will now be set forth.

In the accompanying drawings there is set forth in Fig. 1, diagrammatically, a flow sheet indicating the steps for preparing the improved alumina base for the hydroforming catalyst, and in Fig. 2, a flow plan depicting the essential apparatus of a hydroforming plant.

Referring in detail to Fig. 1, 1 represents a mixing tank provided with a suitable stirrer to which the following are added:—

From storage 3, which contains an aqueous solution of sodium aluminate in a concentration by weight of 20% Al₂O₃ with 8 wt. % excess NaOH, there is charged via line 4 to

tank 1, a quantity of this sodium aluminate material. Simultaneously, from storage 5, there is withdrawn through line 6 and charged to tank 1 a quantity of aluminium sulfate solution. From storage 7, which contains sodium silicate solution, this material is withdrawn through line 8 and also charged to tank 1. Dilution water is also added to the tank 1 from lines 9 and 10, respectively.

- 10 The ingredients listed above are vigorously stirred by causing rotation of agitator 2. The proportions of the aluminum-containing ingredients mentioned above are such that two-thirds of the alumina precipitate comes from the sodium aluminate and one-third from the aluminum sulfate. Sufficient aluminium sulphate or sulphuric acid to adjust the pH of the mixture in tank 1 to about 9—10.0 preferably about 9.5 is added to tank 1 through line 11. The mixture in tank 1 is maintained at a temperature of about 40°—120° F., 60°—80° F. being preferred; and pressure in the tank is atmospheric. Precipitation of the alumina is accomplished in a few minutes, say, 3—5 minutes.

An aqueous slurry containing the precipitated alumina is withdrawn from tank 1 through line 12 and then pumped by pump 13 through line 14 to a filter feed tank 15. The concentration of Al_2O_3 by weight in this feed tank is about 1.2%. The slurry in tank 15 is withdrawn through line 16 and thence pumped by pump 17 through line 18 to a primary filter 19, wherein the said slurry is filtered, and the filter cake comprising the alumina is withdrawn at 20 and charged to a mixing tank 21 provided with driven agitating means 22, and to which tank dilution water is added via line 23. Referring again to filter 19, the filtrate is discarded. The purpose of filtering the slurry is to separate the alumina from excess alkali and other impurities, which alumina is then delivered to tank 21 and mixed with fresh water to facilitate subsequent spray drying.

- 45 The aqueous medium containing the alumina in tank 21 is withdrawn through line 24 and then pumped by pump 25 through line 26 to a mixing tank 27 provided with driven agitating means 28, and to which a further quantity of water is added through line 29. After thorough stirring in 27 (as is accomplished in tank 21), the material is withdrawn from tank 27 through line 30, thence passed through a pump 31, thence passed through line 32, through to a high pressure pump 33, which latter pump delivers the slurry via line 34 to a spray dryer 35.

The succession of dilutions and the filtering step, previously described, serve to remove from association with the alumina, substantially all of the extraneous material (e.g. sodium ions and sulfate ions) so that material delivered to spray dryer 35 contains approximately 5.6 parts percent by weight of total solids, of which 5 parts by weight is Al_2O_3 .

Spray dryer 35 may be of any conventional type. The temperature conditions maintained in the spray dryer to effect the desired dehydration are substantially the following, namely; the inlet temperature is about 800° F. 70 while the outlet temperature is about 300° F. The spray dried alumina is withdrawn through line 36 and delivered to tank 37 provided with a suitable driven agitating means 38, and to which water is added through line 39. Again, 75 the alumina is agitated in the aqueous medium and the resultant slurry is withdrawn through line 40, and pumped by a pump 41, through line 42 into tank 43 provided with driven agitating means 44. The aqueous medium is 80 vigorously agitated for several minutes and the slurry is withdrawn through line 45, passed through pump 46 and line 47 to a wash filtering means 48 where it is contacted with acidified wash water obtained from manifold 49 85 through branch line 50. The washed precipitate is withdrawn from filter 48 through line 51 and charged to the dilution tank 52 provided with a driven stirring means 53 to which tank water is added through line 54. The 90 alumina is again vigorously agitated in this aqueous medium for a few minutes, thence withdrawn through line 55 and pumped by pump 56, through line 57 to a second wash filter 58 on which latter filter it is again treated 95 with the aqueous wash water contained in manifold 49 which is fed to said filter through line 59. The precipitate is withdrawn from the wash filter 58 through 60 and delivered to a dilution tank 61 provided with a driven 100 stirrer 62 and to which dilution water is added through line 63. In this tank 61 the alumina-containing aqueous medium is vigorously stirred for a few minutes (again, say, 3—5 minutes), thence withdrawn through line 64 105 and pumped by pump 65 through line 66 to a third water filter 68 where, again, it is treated with acidified water withdrawn from manifold 49 through line 67. The alumina is withdrawn from wash filter 68 via line 70 and 110 passed through a steam tube dryer 69, and the dry product is finally recovered from line 71 and delivered to storage. It will be understood that any suitable drying means may be employed in lieu of steam tube dryer previously mentioned. It is also pointed out that the acidified wash water in manifold 49 contains sulfuric acid equivalent to 14 gms. calcium sulfate per gallon of liquid.

There is thus indicated by the accompanying schematic flow plan, the succession of steps performed in a preferred method of making an alumina composition also containing silica.

In order further to describe the invention, 125 it is pointed out that in tank 1 dilute aluminium sulfate is mixed with partially acidified sodium aluminate solution. The solution concentrations are adjusted to give a slurry in tank 1 containing about 1.2 wt. % alumina. 130

The quantity of aluminum sulfate or of sulfuric acid added is carefully controlled so as to reach the desired pH of 9-10.

The gel slurry is pumped to a filter feed tank and is dewatered on the filter 19. It is pointed out that the rate of filtering is quite sensitive to the pH of alumina precipitation. For example, at pH values in the range of 10-10.3, it is very difficult to dewater the slurry, and consequently, the pH in the tank 1 must be maintained below 10, and preferably, within the range of from 9-9.5 whereupon the filter rate is greatly increased.

The base prepared as explained above is in the form of microspheres and possesses a hard glassy appearance.

In preparing a hydroforming catalyst the base or carrier may be impregnated with a water soluble molybdenum salt which is, at the same time, heat decomposable. The impregnated base is dried, heated and finally calcined. The amount of molybdenum salt impregnated into the base is such as to give a molybdenum oxide (MoO_3) content of about 10% based on the total weight of the catalyst. As much as 15-20% molybdenum oxide may be added for special catalysts. It will be understood, of course, that other known hydroforming catalysts such as chromium oxide, platinum or palladium may be incorporated into the base prepared as described above. Furthermore, the catalyst may be prepared by dry mixing the active component of the cata-

lyst with the base and heating. The present invention is not limited to a particular method of incorporating the active component of the catalyst into the base and, therefore, any known procedure may be employed.

In Fig. 2 there is shown the essentials of an apparatus in which a continuous hydroforming operation may be carried out employing a fluidized catalyst technique. Referring in detail to Fig. 2, 100 represents a reactor containing a bed of powdered fluidized catalyst extending from grid G to an upper dense phase level L. The hydrocarbon to be hydroformed, say, a virgin naphtha containing 35 vol. % of naphthenes with a relatively small amount of aromatics and a major proportion of paraffin hydrocarbons, is charged to the system via line 101, thence passed through a furnace 102 where it is heated to a temperature of around 950°-1000° F., and thence passed via line 103 into a lower portion of a bed of catalyst C, but above the grid G in reactor 100. Simultaneously, a hydrogen-containing gas in line 104 (this gas is obtained from the product recovery system and commonly referred to as recycle gas) is heated in furnace 105 to a temperature of, say, 1200° F., and thence passed via line 106 into the bottom of reactor 100. This recycle gas usually contains 65-75% hydrogen, the remainder being normally gaseous hydrocarbons. The following conditions are maintained in reactor 100:—

Catalyst	- - - - -	10% molybdenum oxide on disclosed base
Amount of catalyst	- - - - -	0.3 lbs. per lb. of oil in reactor
Catalyst particle size range	- - - - -	(5% less than 30 microns 5% more than 100 microns)
Temperature	- - - - -	900°-950° F.
Pressure	- - - - -	100-350 psig.
Superficial velocity of gasiform material in reactor 100	- - - - -	0.5-1.0 ft. per sec.
Residence time of reactants in reactor 100	- - - - -	30-120 seconds

Under the conditions disclosed above, the desired reaction occurs and the product admixed with hydrogen passes from a dense phase extending from G to L into a light phase suspension of catalyst in gasiform material, extending from L to the top of the reactor. Before discharge from the reactor, the gasiform material is forced through a plurality of gas-solids separators S (one shown) wherein entrained catalyst is separated from the gasiform material and returned to the dense phase through dip pipes d (one shown). The raw product emerges from the reactor 100 through line 107 and thence is charged to the bottom portion of a scrubber 108 wherein it flows countercurrently upward against the down-flowing oil charged to scrubber 108 through line 109. The downcoming oil, which is cooler than the gasiform material charged to the scrubber 108, washes out whatever catalyst is still entrained in the vapors and causes

condensation of the higher boiling polymers present in the crude product. The portion of the product which undergoes condensation, plus the added scrubbing oil, plus the catalyst removed from the gasiform material, is withdrawn as a slurry from the bottom of scrubber 108 through line 110. This slurry may be returned to the reactor 100 or rejected from the system. The uncondensed, gasiform material is withdrawn from scrubber 108 overhead through line 111 and is charged to a product recovery system 112 wherein the "hydroformate" is recovered and hydrogen gas is also recovered for recycle to line 104.

Since the catalyst undergoes contamination by carbonaceous and other deposits during the hydroforming operation in reactor 100, it is necessary to regenerate the catalyst. Toward this end catalyst is withdrawn from the reactor 100 through drawoff line 113 carrying the usual gas taps t and controlled by a valve 114

and charged into a stream of air in line 115 wherein it is formed into a suspension and carried into regenerator 116 where it is formed into a fluidized bed C_1 extending from a grid G_1 to an upper dense phase level L_1 . In a manner entirely analogous to that in which the bed of fluidized catalyst was formed in the reactor 100, the catalyst in regenerator 116 is formed into a second fluidized bed, mainly, by controlling the superficial velocity of the up-flowing regeneration gas. The treatment of the fouled catalyst in regenerator 116, with air or other oxygen-containing gas, substantially frees the catalyst of contaminating carbonaceous and sulfurous deposits, and the regeneration fumes pass from the dense phase into an upper dilute phase extending from L_1 to the top of the reactor. Before the fumes are rejected from the regenerator 116 they are forced through a series of gas-solids separating devices S_1 (one shown) wherein entrained catalyst is separated from the said fumes and returned to the dense phase through a plurality of dip pipes d_1 (one shown). In order to prevent overheating of the catalyst in regenerator 116, a cooling fluid in line 117 is charged to a coil 118 disposed in the bed of catalyst wherein heat is abstracted from the said bed of catalyst, the cooling fluid being withdrawn through line 119. The regenerated catalyst is withdrawn from regenerator 116 through drawoff pipe 120 carrying the usual gas taps t and controlled by a valve 121 and charged into a stream of recycle gas in line 122, wherein it is formed into a suspension and returned to the reactor.

The temperature in the regenerator is maintained between 1150°—1200° F. and the circulation rate of catalyst from the regenerator to the reactor is from 1 to 3 parts of catalyst per part of oil.

If desired, the catalyst may be treated with hydrogen in a separate vessel in the case where the catalyst contains a Group VI metal oxide, such as molybdenum oxide, to partially reduce the said oxide to a lower valency state. Furthermore, water may be added to the catalyst entering the reactor. This water, however, is preferably added to the recycled hydrogen-containing gas so as to provide a concentration of water entering the reactor of some $\frac{1}{4}$ to 1 mol H_2O per 100 mols of H_2 entering the reactor.

In order further to explain the present invention, the following data are set forth.

EXAMPLE I

The catalyst used here was one in which the base consisted of about 97.1 wt. % Al_2O_3 and 2.9 wt. % SiO_2 , which had been prepared according to the present invention. This base carried about 10% MoO_3 based on the total weight of the catalyst and carrier. The catalyst had the following physical characteristics:—

(a) surface area - 135 M^2/g 85
(b) pore volume .48 cc/g

This catalyst is utilized in hydroforming a feed of the following characteristics:—

FEED.		
API	-	56.9 70
Initial boiling point	-	207° F.
10% off at	-	228° F.
50% off at	-	250° F.
90% off at	-	290° F.
Final boiling point	-	334° F. 75

INSPECTION OF FEED.

Aromatics, wt. %	-	10	
Olefins, wt. %	-	0	
Naphthenes, wt. %	-	39	
Paraffins, wt. %	-	51	80
Octane number (research)	-	50.2	
Aniline point ° F.	-	127	

A naphtha feed of the above characteristics was hydroformed in the reaction zone maintained at a pressure of about 200 psig, while maintaining a temperature in said reaction zone of 925° F. Hydrogen was charged to the reaction zone in the amount of about 5000 cubic feet measured to standard conditions per barrel of oil. The concentration of hydrogen in the hydrogen-containing gas was about 65% by volume.

Operating as above indicated to obtain a 95 octane number (research) product, the product had the characteristics indicated in column A below. In column B the same feed stock was treated in exactly the same manner as the feed stock of column A, but in this case a conventional carrier or base was used to support the molybdenum oxide used in both runs. 100

	A	B	
C_8 and higher hydrocarbon fraction, Vol. %	79	78	
C_4 hydrocarbon fraction, Vol. %	7.5	7.5	105
Normally gaseous hydrocarbons, wt. %	10	11	
Carbon, wt. %	0.6	0.8	
Required space feed rate for 95 ON, lbs.oil/hr./lb. catalyst in reactor	0.37	0.26	110
Volatility of C_8 -430° F. fraction at 95 ON:—			
Vol. % off at 158° F.	7	5	
Vol. % off at 212° F.	31	26	115
Vol. % off at 257° F.	64	63	
Vol. % off at 302° F.	92	92	
Gravity of C_8 -430° F. fraction, ° API	47	46	

It can be seen from the immediately foregoing table that the use of the new and improved base or carrier of the present invention has the following advantages:—

- (1) improved liquid yield (less normally gaseous hydrocarbons) 125
- (2) lower carbon
- (3) higher activity
- (4) improved volatility

These advantages are apparent from a study of the table immediately above.

In the fluid operation it is essential that the powdered catalyst have good attrition resistance. In other words, the catalyst must have sufficient mechanical strength to withstand physical disintegration when employed during a process utilizing the fluidized catalyst technique. The data below show that the catalyst A which contains the improved base had superior attrition resistance to the conventional catalyst B, as follows:—

	A	B
Attrition resistance, lbs. of 0—40 micron material formed per day per 100 lbs. of 40+micron material in reactor	0.5	2.0

To recapitulate briefly, the present invention relates to a method for the preparation of microspherical particles of catalyst carriers or bases suitable for use in a hydrocarbon hydroforming reaction carried out by the fluidized solid technique which comprises mixing an aqueous solution of aluminum sulphate with an aqueous solution of sodium aluminate, the hydrogen ion concentration being adjusted to between pH 9 and 10, to form a precipitate, filtering, reslurrying the precipitate with water and spray drying the resulting slurry. The present invention also relates to a method for the preparation of microspherical catalyst particles for a fluidised hydroforming reaction wherein the particles prepared by the method specified above are mixed with a hydroforming catalyst such as molybdenum oxide, chromium oxide, titanium oxide, platinum or palladium. It has been found that the inclusion of a small proportion of an aqueous solution of sodium silicate in the reaction mixture to incorporate silica in the carrier or base greatly improves the catalyst composition for the silica in the carrier yields a catalyst composition of good activity, good selectivity, and also provides a catalyst which in the form of a powder of fluidizable size possesses good resistance to attrition when employed in the form of a fluidized bed in a hydroforming process. The percentage of silica in the carrier may be varied from 0.5 to 5.0% by weight according to the service to which the catalyst is to be subjected or the desired results. The low silica content is used where a minimum degree of hydrocracking of the paraffins is desired. Preferably the carrier should contain between 1 and 5% by weight of silica.

With respect to the proportions of sodium aluminate and aluminate sulfate used in preparing the present catalyst carrier or base, these may vary somewhat from the proportions heretofore given. During several washings of the slurry or precipitate originally formed, the sodium content of the base material was reduced to not more than one-tenth of 1% sodium expressed as NaOH.

As pointed out previously, in preparing a molybdenum oxide-containing catalyst, a good procedure is the so-called "dry-mix" procedure in which molybdenum oxide (MoO_3) is mixed with the proper amount of the present base and heated to a temperature of from 1000°—1400° F., whereupon the molybdenum oxide is vaporized and distributed homogeneously throughout the base material. At the higher temperatures, the incorporation of the molybdenum oxide into the base is accomplished by this procedure in a matter of a few minutes.

Instead of using platinum, palladium or molybdenum oxide, chromium oxide or titanium oxide may be used.

In the case of a platinum-containing catalyst, the intermediate concentrate method is preferably employed, namely, the improved base is impregnated so as to contain, say, 5—10% by weight of platinum and then mechanically mixed with the present base in proportion such that the final mixture will contain from about 0.2—0.5 wt. % platinum based on the total weight of the catalyst.

The catalysts prepared according to the foregoing disclosure have been found to possess greatly improved properties when used in the form of a fluidized bed in a hydroforming operation since tests in a pilot plant unit have demonstrated that the present new catalysts possess high activity, selectivity and resistance to attrition. The method of spray drying the catalyst is instrumental in enabling control of the particle size of the catalyst. The catalyst has also been found to be stable at the high temperatures utilized in regenerating the catalyst and the catalyst has also demonstrated that its activity is maintained for a long period of time.

According to a further feature of the invention the catalyst may be still further improved by adding a water soluble organic compound containing a plurality of hydroxyl groups such as gluconic acid during the preparation of the catalyst base. This has the effect of increasing the density of the catalyst in fluidized state which is important. The best manner in which this may be performed is illustrated in the following examples.

EXAMPLE II.

ALUMINA PREPARED WITHOUT GLUCONIC ACID

To 193 gallons of solution (42% by weight) of sodium aluminate containing 3—4% (by weight) excess caustic and 3 gallons $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$, specific gravity 1.4 diluted with 2300 gallons of water, is added 325 gallons of 25% (by weight) aluminum sulfate solution diluted 4:1 with tap water prior to addition to the batch. The final pH of the batch is 9.5 and a temperature of about 80° F. is maintained during the preparation. The slurry is heated to about 120° F. and filtered. The filter cake is

reslurried with fresh water and filtered several times to remove alkali and finally spray-dried.

EXAMPLE III.

ALUMINA WITH 1.67% GLUCONIC ACID—

BASIC SODIUM ALUMINATE

To 193 gallons of 42% sodium aluminate solution containing 13 pounds of gluconic acid and 3 gallons of sodium silicate, $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2$, specific gravity 1.4, diluted with 2300 gallons of water is added 325 gallons of 25% aluminum sulfate solution diluted 4:1 (by weight) with tap water prior to addition to the main batch. The final pH of the batch is 9.5 and the temperature of the preparation about 80° F. The slurry is heated to about 120° F. and filtered. The filter cake is reslurried with fresh water and filtered several times and finally spray-dried.

EXAMPLE IV.

ALUMINA CONTAINING 3% GLUCONIC ACID— BASIC SODIUM ALUMINATE

To 200 gallons of tap water at about 80° F. is added 1 quart sodium silicate solution $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2$, specific gravity 1.4, 6 gallons of 42% (by weight) sodium aluminate liquor containing 0.405 lbs. of gluconic acid, and 0.325 pounds of gluconic acid added in the form of 50% (by weight) solution. To this solution an aluminum sulfate solution is added which is prepared by diluting 12½ gallons of 25% (by weight) aluminum sulfate solution with 100 gallons of tap water. It requires 55 gallons of this diluted aluminum sulfate solution to adjust the pH of the batch to 9.35. The solution is filtered and the filter cake reslurried, filtered, washed and spray-dried as in the above examples.

The fluid density characteristic of the above carrier or base materials prepared as above and then combined with 10 weight per cent MoO_3 by impregnation with the proper amount of an ammonium molybdate solution, drying and activating for 6 hours at 1200° F., and formed into fluidized beds of the powdered catalyst, each having the same particle size distribution and each bed fluidized

by the same gas flowing through the several beds at the same superficial velocity, gave the below result:—

Catalyst prepared from: II III IV 50
Fluid density, lbs./CF 32 39 39

It will be noted that the catalysts prepared by including gluconic acid in the spacing agent or alumina base possessed an appreciably higher catalyst density than those in which the gluconic acid was omitted. This is an important improvement for the following reason. In determining feed rates to a fluidized bed of catalyst the accepted method is to express the feed rate in unit weights of oil per unit weight of catalyst in the reactor per hour (w/hr./w). In other words, the throughput for a given unit in a given volume of catalyst may be increased by increasing the density of the catalyst. 60

It will be noted that the catalyst prepared using the base as described in Example III above possessed a density which exceeded that of the catalyst prepared containing the base of Example II by over 20%. This means that when employing reactors containing the same volume of catalyst prepared according to Examples II and III, respectively, the throughput, under the same conditions of operation of the reactor containing catalyst in Example III, will exceed the throughput of the reactor containing the catalyst in Example II by over 20% while yielding a product naphtha of the same octane number in each case. 80

In order further to explain the present invention, there is set forth below the results of some catalyst activity tests for, of course, in the preparation of a catalyst wherein the procedure for preparing the catalyst and the ingredients thereof are changed from prior known catalysts, it is necessary to test the activity and selectivity of the new catalyst to determine whether or not the modified procedure in the preparation of the catalyst improves or decreases its catalytic functions. Such tests have been made in fixed bed hydroforming units under the conditions as set forth below with the results of such tests. 85

95 88 Al_2O_3 —2 SiO_2 —10 MoO_3 Catalyst
200 CC. Fixed Bed Hydroforming Units
200°—330° F. Virgin Naphtha, 900° F., 200 Psig., 1 V/V/Hr., 1500 CF/Bbl. H_2 .

	Catalyst Base	Example II	Example III	Example IV
	% gluconic acid in aluminate	0	1.7	3.0
100	Activation Temp., ° F.	1200	1400	1200
	Yields			
	$\text{C}_{10}+$, Vol. % of product (%)	-2	0	-4
	Relative carbon (%)	0.9	0.7	0.5
	Relative gas (%)	0.9	1.1	1.0
105	Relative Activities (%)			
	Calculated by weight	1.0	1.3	0.7
	Calculated by volume	0.9	0.9	1.0
	Fluid density, lbs./cu. ft.	32	39	39

(1) Percentage increase yield given by the catalyst of the examples compared to that given by a standard Al_2O_3 — MoO_3 catalyst at same product aniline point.

(2) Amount of product/amount of catalyst for the catalyst of the examples divided by the similar ratio for a standard Al_2O_3 - MoO_3 catalyst at same product aniline point.

5 These data clearly show the marked increase in fluid density effected by inclusion of gluconic acid in the alumina base as taught by this invention. At the same time, the hydro-
10 forming data show that the use of gluconic acid has no adverse effect on catalyst performance. The increased density would improve the activity in a fluid unit.

What we claim is:—

1. A method for the preparation of micro-
15 spherical particles of catalyst carriers or bases suitable for use in a hydrocarbon hydroforming reaction carried out by the fluidized solid technique which comprises mixing an aqueous solution of aluminum sulphate with an aqueous
20 solution of sodium aluminate, the hydrogen ion concentration of the mixture being adjusted to between pH 9 and 10, to form a precipitate, filtering, reslurrying the precipitate with water and spray drying the resulting slurry.

2. A method as claimed in claim 1 wherein the quantities of materials used are such as to give an aqueous mixture containing about 1.2% by weight of alumina.

3. A method as claimed in claim 1 or 2
30 wherein the hydrogen ion concentration of the mixture of aqueous solutions is approximately pH 9.5.

4. A method as claimed in any of claims 1 to 3 wherein the hydrogen ion concentration is
35 adjusted by the addition of an acid.

5. A method as claimed in any of claims 1 to 4 wherein the hydrogen ion concentration is adjusted by the addition of sulphuric acid.

6. A method as claimed in any of claims 1
40 to 5 wherein the reaction mixture is maintained at a temperature between 40° and 120° F. and preferably between 60° and 80° F. for a sufficient time to form a precipitate.

7. A method as claimed in any of the preced-
45 ing claims wherein a small proportion of an aqueous solution of sodium silicate is also added to the reaction mixture.

8. A method as claimed in any of claims 1 to 7 wherein a small proportion of an aqueous solution of gluconic acid is also added to the
50 reaction mixture.

9. A method as claimed in any of the preceding claims wherein the spray dried precipitate is subjected to a number of consecutive alternate stages of reslurrying and filter
55 washing with aqueous acid solution before final drying.

10. A method for the preparation of micro-spherical catalyst particles for a fluidised hydroforming reaction wherein the particles
60 prepared by the method of any of the preceding claims are mixed with a hydroforming catalyst such as molybdenum oxide, chromium oxide, titanium oxide, platinum or palladium.

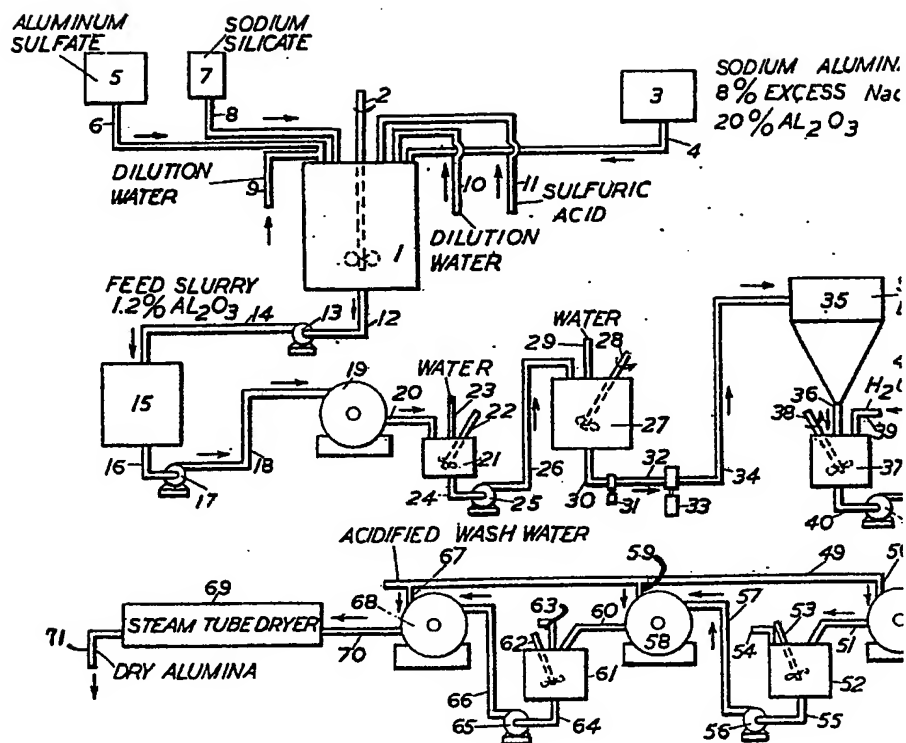
11. A method as claimed in claim 10 wherein the hydroforming catalyst is incorporated
65 by impregnating the dried precipitate with a solution of heat-decomposable salt of the hydroforming catalyst and drying and calcining the impregnated precipitate to convert the
70 salt into the catalyst.

12. A material having a high resistance to attrition and suitable for use as a base for catalysts to be used in reactions carried out by the fluidized solids technique prepared by
75 the methods claimed in any of claims 1—9.

13. A catalyst suitable for hydroforming reactions carried out according to the fluidized solids technique when prepared by the methods
80 claimed in claims 10 or 11.

14. A process for hydroforming naphthas which comprises contacting the said naphthas under hydroforming conditions of temperature pressure and residence time and in the presence of hydrogen with a fluidized bed of a
85 hydroforming catalyst carried on a support prepared by the methods claimed in any of the above claims 1—9.

K. J. VERYARD,
33, Davies Street,
London, W.1,
Agent for the Applicants.



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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

FIG. 2.

SODIUM ALUMINATE
8% EXCESS NaOH
20% AL_2O_3

4

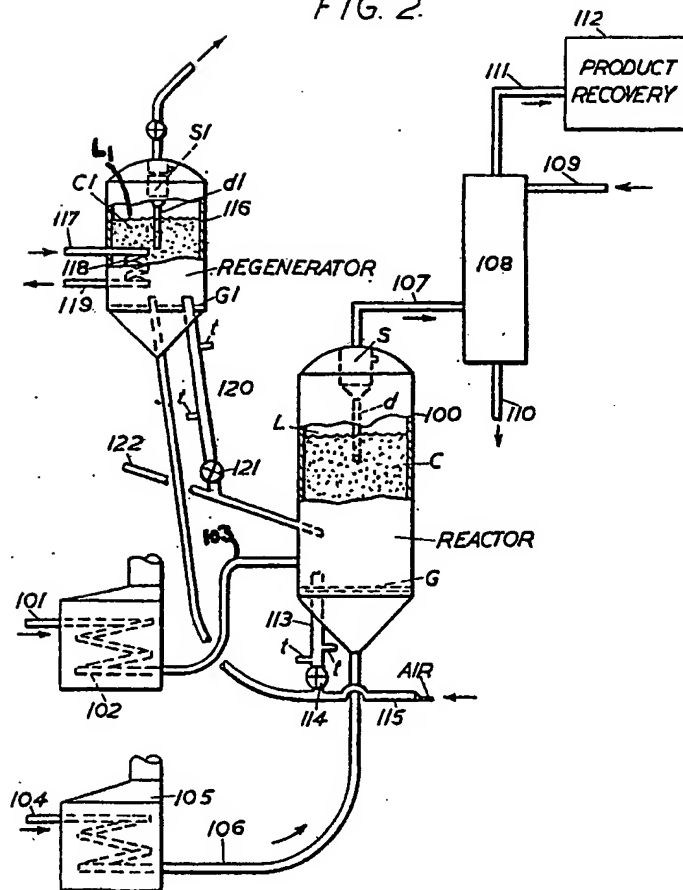
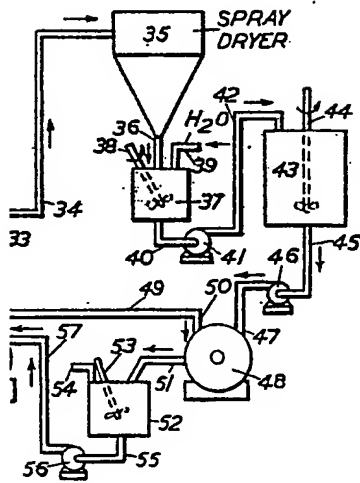


FIG. 1

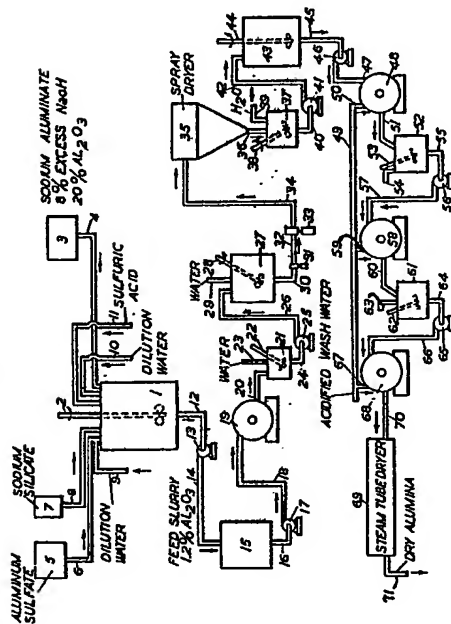


FIG. 2

